

NEW METHOD OF CONSTRUCTING THE 1-PYRAZOLINE RING

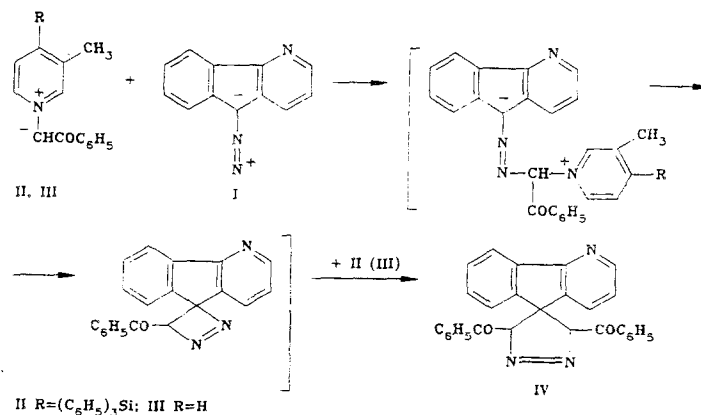
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UDC 547.778'836.07

The preparation has been reported [1] of a substituted pyridazotriazine by 1,3-dipolar cycloaddition of benzyldiazomethane to pyridazinium benzyldiazomethide. We have found that the reaction follows a different course when equimolar amounts of 9-diazo-4-azafluorene (I) and 3-methyl-4-(triphenylsilyl)- and 3-methylpyridinium benzyldiazomethides (II and III) are allowed to react in chloroform at 20°C for 5 h. The ylids (II) and (III) were generated from the N-phenacylpyridinium bromides with 40% aqueous potassium carbonate in chloroform at 20°C. The ylid (II) gave a 35% yield of 3',5'-dibenzoylspiro[4-azafluoren-9,4'-(1-pyrazoline)] (IV) as canary yellow crystals, mp 164-166°C (from heptane-ethyl acetate). IR spectrum (KBr): 1690 cm^{-1} (CO). PMR spectrum (C_6D_6), Z-isomer: 8.84 (1H, dd, 1-H), 8.54 (1H, dd, 3-H), 7.25 ppm (1H, q, 2-H). The signal for the 8-H proton overlapped the signals for the aromatic protons at <7.5 ppm; E-isomer: 8.66 (1H, br.d, 8-H), 8.38 (1H, dd, 3-H), 7.96 (1H, dd, 1-H), 6.82 (1H, q, 2-H), 6.20 and 6.21 ppm (2H, s, 3'-H and 5'-H). Mass spectrum m/z (intensity, %): 429 (26), 324 (22), 296 (16), 179 (26).

The ylid (III) gave 32% of (IV). In both syntheses, approximately 50% of the diazo-compound (I) was recovered. In the case of (II), 3-methyl-4-(triphenylsilyl)pyridine was isolated from the reaction mixture (63% yield). In these reactions, the pyridinium ylids (II) and (III) are donors of the phenacylidene group, which is involved in the formation of the 1-pyrazoline ring.

The reaction is presumed to proceed as follows:



According to the PMR spectrum, the benzoyl groups in the pyrazoline ring in the spiro-compound (IV) are located in the cis-positions, and the compound is a mixture of the Z- and E-isomers (1:1 ratio) with respect to the disposition of the benzoyl groups relative to the pyridine ring of the azafluorene fragment.

LITERATURE CITED

1. I. Zugravescu and M. Petrovanu, *Chimia N-ilidelor*, Ed. Acad. Sci. Rep. Soc. Rom., Buc. (1974), p. 241.

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